5-1-1970

A Study of Substituent Effects in Selected Aromatic Systems by Nuclear Magnetic Resonance Spectroscopy

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A STUDY OF SUBSTITUENT EFFECTS IN SELECTED AROMATIC SYSTEMS BY NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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May 1, 1970

Submitted to the faculty of Ursinus College
in partial fulfillment of the requirements for
Departmental Honors in Chemistry

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TABLE OF CONTENTS

I. INTRODUCTION

Many chemical investigations have been devoted to determining the effect of the addition of certain substituents on the nature of a parent molecule. It was quickly realized that the same substituent appeared to affect more than one system in a similar manner and that these effects appeared to be related to the electronic character of the substituent.

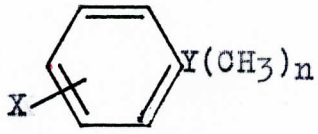
Suspecting that these substituent effects could be subjected to a more quantitative treatment, Louis Hammett turned to a study of substituted benzoic acids. The dissociation constants of such acids were found greater or less than that for unsubstituted benzoic acid, depending on the nature of the substituent. Hammett defined a constant, sigma, such that $\sigma = \log K_s/K_u$ where K_s = dissociation constant of the substituted acid and K_u = dissociation constant of benzoic acid. Positive values for σ were, therefore, assigned to groups that enhanced acidity, or to those groups that attracted electron density. Negative values for σ were obtained for groups that decreased acidity, or donated electron density to the aromatic system.

By applying these newly defined sigma constants to other aromatic systems, such as the dissociation of phenylacetic acids, he found that $\log K_s/K_u = \rho\sigma$ where K_s is the acid dissociation constant for the substituted acid, K_u for the unsubstituted parent, σ is the constant defined from the benzoic

acid series, and ρ is a constant characteristic of the series. Thus, a plot of log K_s/K_u versus σ for each system yielded a straight line whose slope, ρ, provided a measure of the sensitivity of the particular series to changes in substituent groups--the greater the slope, the more profound the effect.

Recognizing the utility of presenting data involving substituent effects in such a linear manner, other workers began to test this correlation of σ constants with various types of measurements.[2] Other equilibrium constants (K) as well as rate constants (k) were equally well-handled by such an approach. Not only these reaction parameters, but also spectroscopic parameters, like infrared absorption intensities, involving the physical rather than chemical nature of the molecules were also found linearly related to these substituent constants.

Nuclear magnetic resonance (nmr) spectroscopy parameters appear to reflect the electronic nature of the absorbing center; thus, substituents might be expected to systematically alter the value of these parameters. A broad investigation of such substituent effects on nmr parameters has been undertaken jointly by Ursinus and Franklin and Marshall Colleges in systems of the types:



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These studies have been undertaken to determine if certain nmr parameters can be correlated with Hammett σ constants. The particular parameters include: 1.) Chemical shifts (δ) of the α-methyl groups in compounds of type 1; 2.) Carbon-13 proton coupling constants ($J_{C^{13}H}$) of these same methyl groups; and 3.) the "internal chemical shift" (Δ) of the α-ethyl groups in compounds of type 2. If these nmr parameters can be found dependent on these σ constants, then the slope of the resulting linear plots can be evaluated in terms of the relative abilities of the particular Y atoms studied to pass on substituent effects to attached groups. The greatest slope would result from the series whose heteroatom possessed the greatest "transmittivity," a property which would be expected to depend on the ability of the particular atom to interact with the aromatic electron system.

In systems of type 1, the chemical shift (δ) of the α-methyl group(s) is a function of the electronic environment of the absorbing proton.[3] If diamagnetic shielding is considered, then an electron-withdrawing group (positive σ constant) will remove electron density from the absorbing center, reducing the magnitude of the field induced to oppose the applied magnetic field. These "deshielded" protons will then absorb at a lower field strength, or show a greater chemical shift relative to tetramethylsilane (TMS) than those in molecules without such a substituent. Thus, chemical shift data plotted versus σ constants might be expected to show a

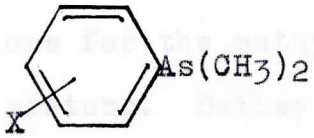
linear relationship with a positive slope whose magnitude can be interpreted as a reflection of the ability of the particular "Y" atom to transmit substituent effects.

Several groups of workers have explored such chemical shift--Hammett relationships with good results for substituted anisoles,[4] toluenes,[4] tert.-butylbenzenes,[5] and N,N-dimethylanilines.[6] In studies recently carried out jointly at Ursinus and Franklin and Marshall, Yoder, Tuck, and Hess[7] investigated toluenes, anisoles, tert.-butylbenzenes, and N,N-dimethylanilines while this author[8] last year commenced a study of arylmethylsulfides and aryldimethylphosphines.

These chemical shift relationships have been found solvent dependent. Since the above-mentioned aryldimethylphosphines could not be studied in carbon tetrachloride, the solvent previously used, benzene was employed. The chemical shift versus σ plot for this data resulted in a line with good correlation; however, the slope was negative in value with a magnitude much greater than that observed for the other series.[8] Bowie, Ronayne, and Williams[9] observed a similar change in slope for a series of substituted anisoles which they attributed to either a charge-transfer or dipole-induced dipole complex between benzene and the solute molecule. Since chemical shifts are affected by any changes in electronic environment, such a complex, which would result in greater electron density, depending on the strength of the complex, would be expected to markedly affect the chemical shifts in

these systems.

This project seeks to extend the study of $\underline{\xi}$-$\underline{\sigma}$ relationships to aryldimethylarsines (type 3) and to further those begun for arylmethylsulfides (type 4) and aryldimethylphosphines (type 5):



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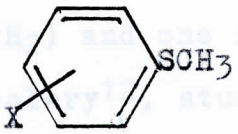

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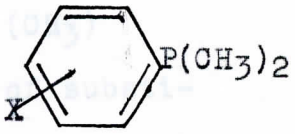

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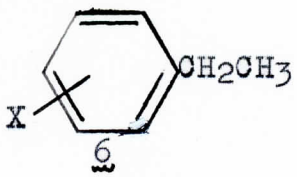
The effect of various solvents on these relationships is also explored.

Carbon-13 proton coupling constants (J) have been shown related to the s character of the C-H bond and to the effective nuclear charge.[10] According to Bent's isovalent hybridization model[11], an electron-donating substituent (negative σ value) decreases the effective electronegativity of the entire aromatic system to which the methyl group is attached in systems of type 1. This decreased electronegativity would result, in turn, in decreased s character and nuclear charge in the C-H bonds and, therefore, in a smaller coupling constant. The work carried out here and at Franklin and Marshall[7,8] represents the first attempts to relate $J_{C^{13}H^1}$ with Hammett σ constants and has resulted in successful correlations. Since coupling constants should be relatively free of solvent or anisotropy effects, such J versus σ plots might better reflect substituent effects than the plots involving chemical shift data in

which such complications cannot be entirely eliminated. This project also involves an extension of such coupling constant investigations to the arsenic system (type 3) and a continuation of that begun last year on the phosphorus (type 5) and sulphur (type 4) series.

In systems of type 2, two chemical shifts can be determined--one for the methylene (CH_2) and one for the methyl (CH_3) protons. Dailey and Shoolery[12], studying a series of substituted ethanes, have suggested that the difference between these two values, called the "internal chemical shifts," is a reflection of the electron withdrawal of an attached substituent. Thus, in aromatic systems of type 2, it might be expected that this internal chemical shift (Δ) should also be related to Hammett σ constants in a manner analagous to that found for chemical shifts and coupling constants. These Δ-σ plots might also serve as an effective means of eliminating anisotropy considerations. Since both the methylene and methyl groups should experience similar anisotropy effects, the subtractive process used to obtain Δ should negate these effects. This project represents an attempt to establish Δ versus σ relationships for ethyl benzenes (type 6), phenetoles (type 7), N,N-diethylanilines (type 8), and aryldiethylphosphines (type 9):



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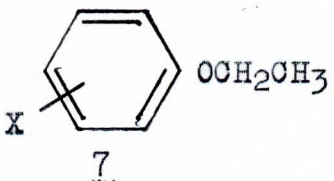

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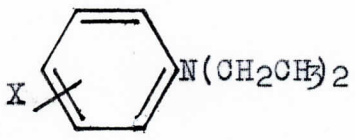

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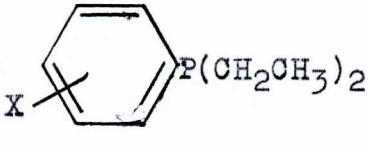

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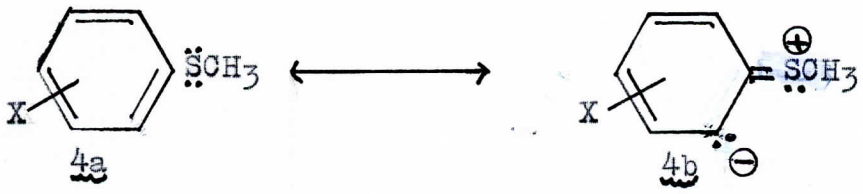
A comparison of the various types of correlations of nmr parameters with σ constants for each of the series should provide a means for evaluating not only the relative transmittivities of the atoms studied, but also the various methods employed to study these effects. Once satisfactory correlations have been obtained for the various series examined, then the effect of substituents previously unstudied can be evaluated by employing these groups as substituents on any of these series. Not only can qualitative statements be made by comparing the substituted compound's parameters with those for the unsubstituted parent of the series, but also more quantitative evaluations may be made by using regression analysis values to determine appropriate σ constants for these groups.

Such substituent investigations can provide an indication of the types of bonding employed in these systems, especially for series involving elements of the second or third row of the periodic table (sulphur, phosphorus, arsenic). In such systems, two types of resonance interactions might be possible--$(\underline{p}\text{-}\underline{p})_{\pi}$ type interactions, also operable for the first row oxygen and nitrogen analogs, which involve an unshared pair of electrons from the heteroatom:



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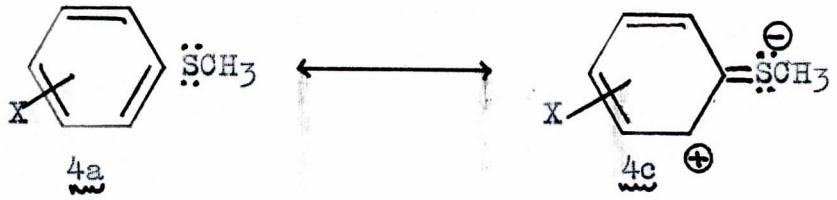
and $(\underline{p}\text{-}\underline{d})_{\pi}$ interactions, not operable for first row elements,

which formally place two of the aromatic electrons into the empty d orbitals of the heteroatom:



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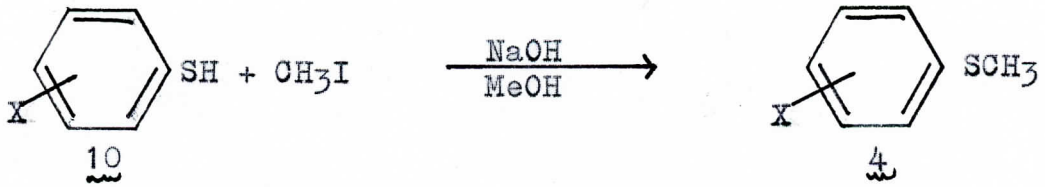
The nmr data might provide a clue as to the relative importance of these two types of interactions.

II. SYNTHESIS

The compounds used in this study that were obtained commercially were assumed pure since they showed no spurious signals in their nmr spectra. Most of the arylmethylsulfides (type 4), aryldimethylphosphines (type 5), and aryldimethylarsines (type 3) were prepared as part of the College Scholars' Project[8] and the details of these preparations were included in that report; only the general methods for these compounds are summarized here. Several aryldimethylphosphines (type 5), aryldiethylphosphines (type 9), phenetoles (type 7), and diethylanilines (type 8) were prepared as part of this project.

The arylmethylsulfides (4) had been prepared in a relatively straightforward manner involving methylation of the appropriate commercially available mercaptans using methyl iodide in the presence of sodium hydroxide and methyl alcohol:



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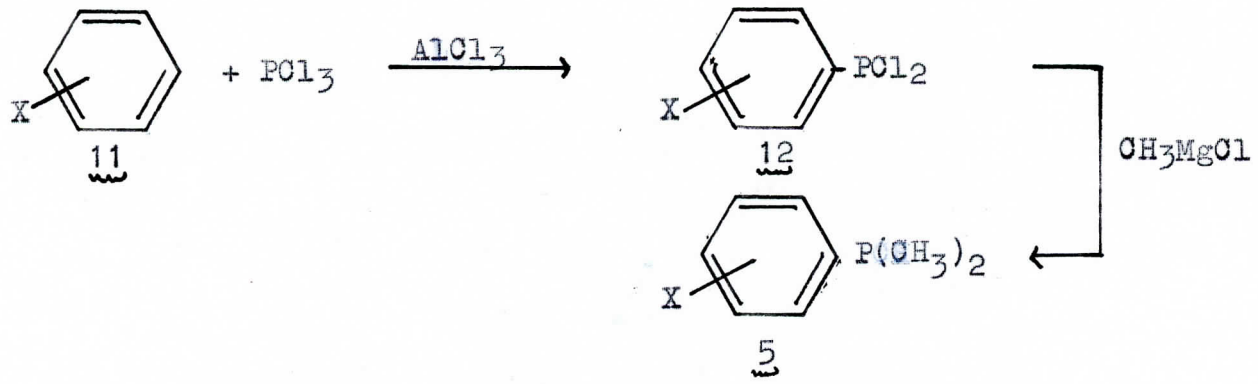
After two hours of reflux, the product was isolated with little contamination from by-products. No effort had been made to maximize yields, but isolation of 50% or more was not uncommon. Only the p-t-butylphenylmethylsulfide appeared to be of new composition, not previously reported in the literature. Prepared in this manner were the following members of the series: p-OCH_3, p-CH_3, m-CH_3, p-$C(CH_3)_3$, p-Cl, p-Br, p-NO_2.

The preparation of the odiferous aryldimethylphosphines (5) had proved more challenging:



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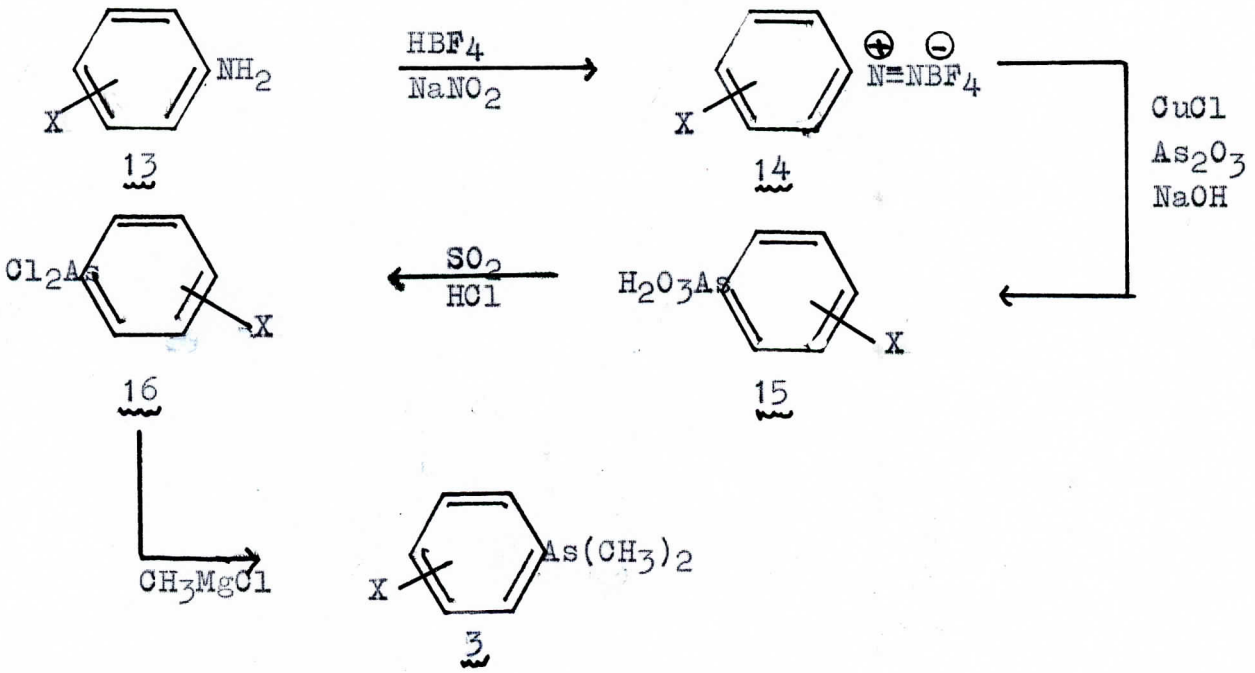
The difficulty lay in the successful preparation of the phosphonous dichloride, a task which was not made easier by the questionable nature of some of the early literature. The procedure was suggested by Michaelis[13] in the late nineteenth century and involved a modified Friedel-Crafts reaction. An apparent complexation between aluminum chloride and the water-sensitive product made isolation difficult. Later workers suggested the use of various complexing agents like phosphorus oxychloride[14] or pyridine[15] to improve the yield. The proper choice of catalyst (aluminum chloride, ferric chloride, or none) and the molar ratio of reactants were apparently critical for success; however, no one set of conditions could be applied to most of the members of the series. Early workers ignored the formation of anything but the para isomer in this Friedel-Crafts reaction. More recent work[16] involving infrared data, indicated that the quantities of the ortho and meta isomers are negligible.

The phosphonous dichlorides were readily converted to the dimethylphosphines through an exothermic treatment with

methylmagnesium chloride in tetrahydrofurane (THF). No evidence for the prior synthesis of some of these compounds could be found. Previously prepared members of the series included: p-H, p-Br, p-Cl, p-CH_3, p-OCH_3, p-$N(CH_3)_2$.

Using methods analogous to those employed for p-methoxyphenyldimethylphosphine and p-N,N-dimethylanilyldimethylphosphine, two additional members of the series were prepared--p-ethoxyphenyldimethylphosphine and p-N,N-diethylanilyldimethylphosphine. Several aryldiethylphosphines were prepared from the previously synthesized arylphosphonous dichlorides. This involved, as for the dimethylphosphines, the slow addition of the phosphonous dichloride to a chilled solution of ethylmagnesium chloride in THF. Two to three hours of reflux proved sufficient for conversion.

The aryldimethylarsines had been prepared through a four-step synthesis starting with the appropriate aromatic amine:



The amine was converted to the diazonium fluoroborate salt (14) and then to the arsonic acid (15) employing the procedures of Organic Syntheses[18] and Organic Reactions.[19] Treatment with sulphur dioxide and hydrochloric acid following the suggestions of Mann, et. al.[19] and Morgan, et. al.[20] produced the dichloroarsine (16) in low yield.

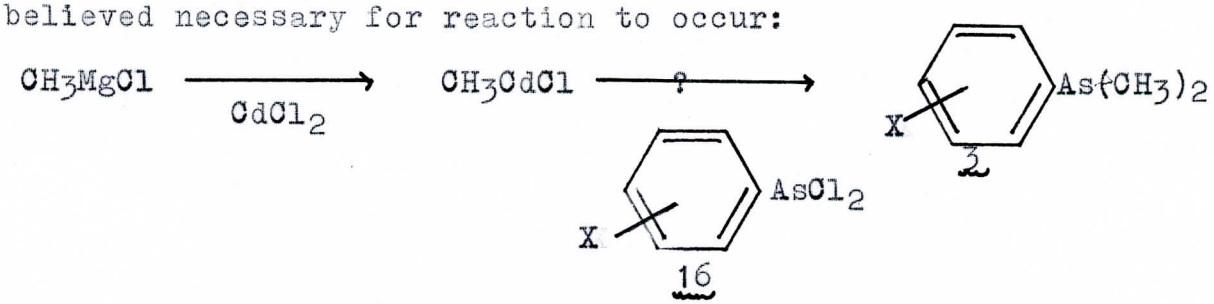
An unusual phenomenon had been noted for two members of the series. The p-methoxy and p-ethoxy phenylarsonic acids upon treatment with sulphur dioxide yielded two substances--the desired dichloroarsine and a lower boiling fraction which had passed through subsequent methylation unchanged and whose spectral and physical data had been consistent with that of anisole (11% yield) and phenetole, respectively. This apparent carbon-arsenic bond cleavage had not been reported in the literature.

Upon treatment with methylmagnesium chloride in THF, the aryldichloroarsine afforded the foul-smelling aryldimethyl-arsines (3), many of which were apparently new compounds. The members of the series produced in this manner included: p-OCH_2CH_3, p-OCH_3, p-CH_3, m-CH_3, p-H, m-OCH_3, p-Cl, m-Cl, p-Br, m-Br.

Methylmagnesium chloride, however, could not be used with several dichloroarsines containing substituents representing the extremes of the sigma scale. For instance, a p-nitro substituent (σ = 0.778; σ^* = 1.270) oxidizes a Grignard while a p-carboethoxy group (σ = 0.522; σ^* = 0.678) reacts to form

an alcohol. Also, the p-dimethylamino (σ = -0.600) compound could not be prepared in the "usual manner" since the starting amine was not readily available commercially or synthetically. Therefore, alternate routes of synthesis, suggested by Chernokal'skii, Gel'fond, and Kamai[21] were tried with, however, little apparent success.

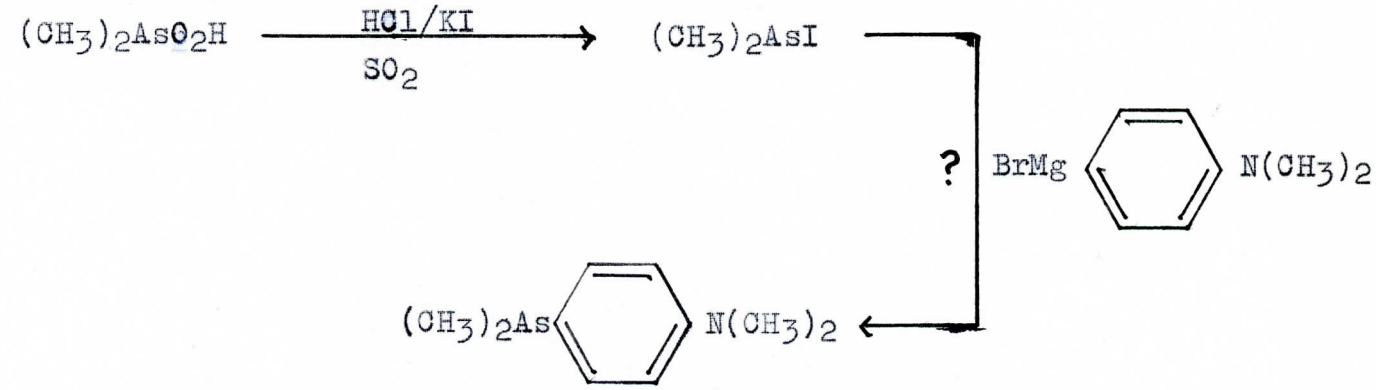
The attempted preparations of p-nitrophenyldimethylarsine and p-carboethoxyphenyldimethylarsine involved the preparations of the corresponding dichloroarsines (16) following the scheme described for the other members of the series. However, the methylation employed methylcadmium chloride[22], an organometallic compound which should not be destroyed by nitro groups or react with carbonyl functions. This reagent is prepared by the addition of anhydrous cadmium chloride to a solution of the methyl Grignard; the resulting magnesium salts are believed necessary for reaction to occur:



In both cases (X = p-NO_2; p-$COOCH_2CH_3$) reaction appeared to occur as expected and a yellow solid was isolated and purified by recrystallization. However, the compounds failed to dissolve in carbon tetrachloride for nmr analysis and an elemental analysis for the supposed p-carboethoxyphenyldimethylarsine apparently ruled out this structure: Carbon: Theo. - 51.93%;

Found - 25.73%. Hydrogen: Theo. - 5.99%, Found - 1.54%.

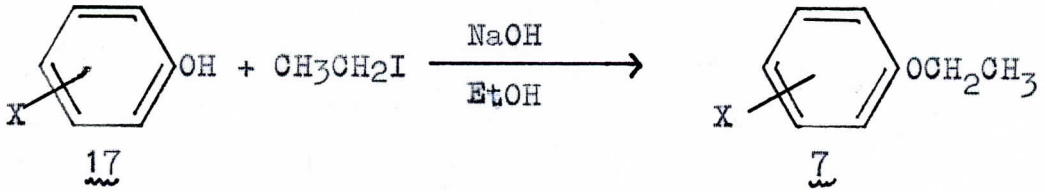
The proposed preparation of p-dimethylanilyldimethylarsine involved the reaction of dimethyliodoarsine (from the reduction of cacodylic acid) with the Grignard reagent freshly generated from p-bromo-N,N-dimethylaniline:



The physical properties of the dimethyliodoarsine synthesized agreed closely with literature values[23]. Thus, the isolation from the final reaction, on two succeeding trials, of only a substance whose data was consistent with that of p-bromodimethylaniline suggests that little or no Grignard had been generated. Apparently, difficulty in producing the reagent is not to be unexpected.[24]

All of the sulfides, phosphines, and arsines possessed strong, unpleasant odors; those of the latter two series were somewhat similar but not identical. Also, a slight, but noticeable difference between the dichloro and dimethyl compounds in these series could be detected. No systematic variation in smell with substituent change was noted. In addition, the dichloroarsines were found to be extreme skin irritants.

The phenetoles (7) were prepared using a method analogous to that for the arylmethylsulfides in which the proper phenol (17) was treated with ethyl iodide in the presence of sodium hydroxide and ethanol:



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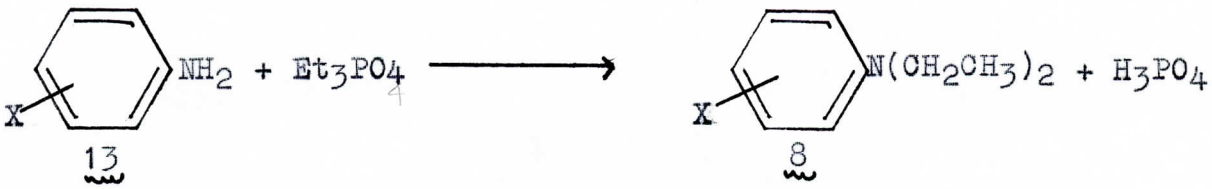
However, for these phenetoles, reaction periods of two to three hours, sufficient for the conversion of the sufficient for the conversion of the sulfides, failed to produce the desired product. By employing reflux periods of two or three days, complete ethylation was obtained. The end of the reaction was generally marked by a color change in which the dark color of the initial phenolate anion was considerably reduced in intensity and altered in hue.

The procedure of Thomas, Billman, and Davis[25] was used to prepare the N,N-diethylanilines:



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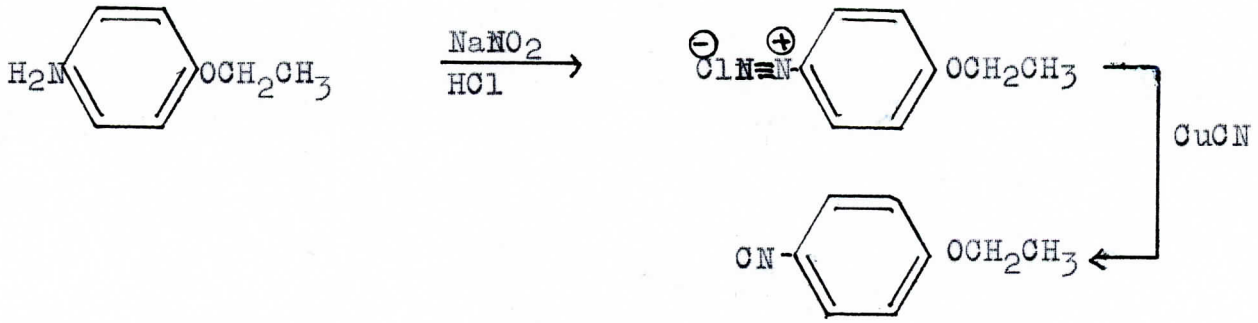
The gentle heating of an excess of triethylphosphate with the appropriate amine produced an exothermic reaction. After two hours of reflux, followed by hydrolysis, the product was extracted and isolated. An attempt to apply this method to iodoaniline, however, resulted in the loss of iodine and the preparation of N,N-diethylaniline.

The preparation of p-ethoxybenzonitrile followed a traditional Sandmeyer procedure[26] using cuprous cyanide and phenetidine:



Care, however, must be exercised to neutralize any acidity before the addition of cuprous cyanide to prevent the liberation of hydrogen cyanide.

III. EXPERIMENTAL

p-Ethoxyphenylphosphonous dichloride was synthesized by a procedure that closely followed that suggested by Gefter[27] for the p-methoxy analog. In a 1-liter, 3-necked flask fitted with a Talboy mechanical stirrer and Friedrichs condenser (arranged so that an HCl exit hose led directly to the hood) was placed anhydrous ferric chloride (60.0 g; 0.37 mole), phosphorus trichloride (114 g; 0.84 mole) and phenetole (103 g; 0.84 mole). The resulting brown mixture was refluxed for four hours after which the orange mixture was stirred overnight without heat. An additional reflux period of two hours was followed by extraction with petroleum ether (30 - 60°C; total volume = 400 ml) in several portions. Removal of solvents at atmospheric pressure left behind a yellow liquid which when subjected to vacuum distillation (employing a Vigreux column 4" long and wrapped with a heating-tape) yielded p-ethoxyphenylphosphonous dichloride, bp 123-26°/0.35 torr (lit.[13] bp 266°), (32.7 g; 17.5% yield).

p-Ethoxyphenyldimethylphosphine was prepared in the following manner. A 500 ml, three-necked flask, fitted with a magnetic stirrer, pressure-equalizing dropping funnel, and efficient west condenser with calcium chloride drying tube had added to it methylmagnesium chloride (68 ml of 2.2 M in THF; 0.15 mole; Fisher Scientific Company). The flask was placed in an ice-bath and p-ethoxyphenylphosphonous dichloride

(13.0 g; 0.058 mole) was added dropwise with extreme caution. Six hours of reflux was followed by the dropwise addition of sat. ammonium chloride solution (~50 ml), again employing the ice-bath. Extraction with solvent ether in several portions (total volume = 400 ml) and atmospheric distillation left a foul-smelling liquid. This, upon vacuum distillation (4" heating-tape wrapped Vigreux column) produced the clear, colorless product, bp 108-110°/2.1 torr, (7.8g, 73%). No evidence for the prior synthesis of the phosphine could be found.

p-N,N-diethylanilylphosphonous dichloride was synthesized in a manner suggested by Viout?[28] In a 500 ml flask equipped with a west condenser and calcium chloride drying tube (with an HCl exit hose leading directly to the hood) was placed N,N-diethylaniline (112g; 0.75 mole; Eastman Chemical mono-free) and phosphorus trichloride (101 g; 0.75 mole). The yellow mixture was placed on a steam bath for six hours during which time the mass solidified. Extraction with several portions of petroleum ether (30 - 60°) left behind a large quantity of white solid (~70g). This solid proved not to be the desired material since subsequent methylation produced only a substance whose data resembled that of diethylaniline. Solvents were removed from the petroleum ether extracts by atmospheric pressure distillation. Repeated attempts at in vacuo distillation failed due to continual clogging of the apparatus. Infrared spectra of the non-distilled semi-solid

material suggested that the product was present.

p-N,N-diethylanilyldimethylphosphine was prepared in a manner analogous to that used for p-ethoxyphenyldimethylphosphine. p-N,N-diethylanilylphosphonous dichloride (~10g) in dry ether was treated with methylmagneisum chloride (114 ml of 2.2 M in THF; 0.25 mole) to give the dimethyl phosphine, bp 113-115/1.5 torr (2.8 g.). This compound could not be found in the literature.

Phenyldiethylphosphine, p-chlorophenyldiethylphosphine, p-ethoxyphenyldiethylphosphine, and p-N,N-diethylanilyldiethylphosphine were prepared by treatment of the appropriate phosphonous dichlorides with ethylmagnesium chloride in THF using the procedure outlined above for the dimethylphosphines. The boiling points and yields for these compounds are as follows: p-H, bp 74-76/2.9 torr (lit.[29] 96-97/10torr), 52%; p-Cl, bp 104-106/2.2 torr (lit.[30] 129-130/15 torr), 25%; p-NEt_2, bp 120-124/2.8 torr; p-OEt, 115-118/0.65 torr (lit.[13] bp 275/atm. press.), 71%. Only the p-NEt_2 compound appeared to be of new composition.

Dimethyliodoarsine (cacodyl iodide) was prepared by the method of Burrows and Turner.[23] Cacodylic acid (25.0g; MC&B technical grade, 65% min.; 0.18 mole if 100%), potassium iodide (80g; 0.48 mole) and water (100 ml) were placed in a three-necked flask equipped with magnetic stirrer, sulphur dioxide inlet tube, and west condenser with gas exit tube. (A trap was used between the gas tank and reaction vessel.)

The solution was saturated with SO_2 by bubbling for ten minutes, then dilute HCl (50 ml conc. HCl, 50 ml H_2O) was added over a twenty minute period producing a red color. Overnight stirring with occasional periods of sulphur dioxide addition resulted in the formation of a red oil and a yellow aqueous layer. The oil was distilled at atmospheric pressure using the 4" heating-tape wrapped Vigreux column yielding the yellow product, bp 155-157 (lit.[23] 154-157), (13.0 g; 31% yield).

The reaction of dimethyliodoarsine with p-N,N-dimethylanilylmagnesium bromide was carried out in the following manner.[21] A 250 ml, three-necked flask with magnetic stirrer, dropping funnel, west condenser, and nitrogen inlet was flame dried and purged with nitrogen. The flask was filled with magnesium turnings (1.5 g; 0.63 mole) and anhydrous ether (25 ml freshly distilled from calcium hydride). p-Bromodimethylaniline (12.0 g; .063 mole) in 50 ml Et_2O was placed in the dropping funnel and a few ml added to the flask. Since no spontaneous reaction occurred before or after the addition of a trace of iodine, "activated magnesium" (prepared by the small scale reaction of ethyl bromide on magnesium in ether) was added. After addition of the amine was complete, the mixture was refluxed three hours. The solution was chilled and dimethyliodoarsine (13.0 g; 0.056 mole) was added during fifteen minutes; stirring was continued for 72 hours at room temperature. To the ice-cold mixture was added dropwise

saturated ammonium chloride solution (~60 ml), followed by extraction with ether. From these extracts was isolated a solid (mp 50 - 52) whose spectrum resembled that of p-bromo dimethylaniline (mp 55).

p-Nitrophenyldichloroarsine was prepared in an apparatus similar to that employed for dimethyliodoarsine. In the flask was placed p-nitrobenzenearsonic acid (25.0 g; 0.10 mole), potassium iodide (a trace), and conc. HCl (220 ml). Sulphur dioxide was passed through the stirred solution for two hours after which the mixture was extracted with three portions of benzene (total volume = 300 ml). The orange extracts were distilled at atmospheric pressure, then fractionated in vacuo on a Vigreux column. The product was collected as a red oil, bp 178-80/0.23 torr (lit.[19] bp 189/0.4 torr), (22.2 g; 82%).

The reaction of p-nitrophenyldichloroarsine with methylcadmium chloride according to the procedure of Chermokal'skii, Gel'fond, and Kamai[21] was carried out in an attempt to synthesize p-nitrophenyldimethylarsine. In a one-liter flask, fitted with dropping funnel, magnetic stirrer, west condenser, and nitrogen inlet was placed anhydrous ether (100 ml freshly distilled) and magnesium turnings (4.8 g; 0.20 mole). After this mixture was cooled on an ice-bath, methyl iodide (28.4 g; 0.20 mole) was added at such a rate that reflux was maintained. The reagent was boiled one hour during which time it turned dark green. To the ice-cold Grignard was added anhydrous cadmium

chloride (36.6 g; 0.20 mole; freshly dried in 110° oven) over a fifteen minute period. This thick mixture, to which additional ether had been added, was refluxed three hours. While again using an ice-bath, p-nitrophenyldichloroarsine (22.2 g; 0.082 mole) was dropped in and refluxing was continued two hours, then stirred at room temperature overnight. To the chilled mixture was added dilute HCl (10 ml con. HCl; 35 ml H_2O). Three portions of ether were used to extract the product. After evaporation of solvents, the remaining oil slowly solidified. The material was recrystallized from benzene (160° C. d.) to give a yellow powder of unknown composition.

A similar procedure was used in an attempt to prepare p-carboethoxyphenyldimethylarsine. p-Carboethoxyphenylarsonic acid was reduced with sulphur dioxide and hydrochloric acid to give p-carboethoxyphenyldichlorarsine. Treatment of this dichloroarsine with methylcadmium chloride yielded an unknown yellow product (135° d.).

p-Ethoxyanisole was prepared in the following manner. A 250 ml flask was equipped with magnetic stirrer, dropping funnel, and west condenser. Sodium hydroxide (3.1 g; 0.078 mole) dissolved in a minimum of water, then diluted with ethanol (100 ml) was added to the flask with p-methoxyphenol (10.0 g; 0.078 mole). Ethyl iodide (15.6 g; 0.10 mole) was added dropwise over a thirty minute period resulting in an orange solution which was refluxed briskly for 28 hours. The light yellow solution was evaporated which left behind a dark

solid material. Two recrystallizations from ethanol/water produced white crystals, mp. 33.5-34.5 (lit.[31] mp 36-37).

m-Diethoxybenzene, p-diethoxybenzene, and p-ethoxyacetophenone were similarly prepared in good yields; the two diethoxy compounds involved the addition of two equivalents of ethyl iodide to resorcinol and hydroquinone, respectively. The physical data for these compounds is as follows: m-OEt, bp 105-106/0.65 torr (lit.[32a] bp 234-235/atm. press.); p-OEt, mp 70-72 (lit.[32b] mp 71-72); p-CH_3CO, mp 34-36 (lit.[32c] mp 36-37).

p-Ethyl-N,N-diethylaniline was prepared by the method of Thomas, Billman, and Davis.[25] A one-liter flask with west condenser was filled with p-ethylaniline (25.0 g; 0.206 mole) and triethylphosphate (37.5 g; 0.206 mole). The mixture was heated gently with a bunsen burner until reaction commenced. After the spontaneous boiling had ceased, the burner was returned and the two phase solution refluxed gently for three hours. To the cooled flask was added a magnetic stirrer. The mixture was hydrolyzed with NaOH solution (8.4 g; 0.21 mole in 200 ml water) overnight. The aqueous layer was extracted with four portions of ether (total volume = 250 ml). Removal of solvent left a liquid which was fractionated *in vacuo* on a Vigreux column to give the clear product, bp 82-85/1.0 torr (16 g; 44%).

N,N,N',N'-tetraethylphenylenediamine, p-N,N-diethylphenetidine, and p-N,N-diethylaminoacetophenone were prepared in a similar fashion. The data for these compounds is as

follows: p-NEt_2, mp 48.5-49.5 (lit.[32d] mp 52); p-CH_3CO, molecular distillation 150/1.9 torr (lit.[33] mp 47-48); p-OEt, bp 121-23/3.0 torr.

p-Ethoxybenzonitrile was prepared according to the method of Clarke and Reede[26]. A one-liter flask fitted with mechanical stirrer, thermometer, and condenser was placed in an ice-bath and in it was placed cuprous cyanide (32.4 g; 0.36 mole), water (150 ml), and benzene (100 ml). The temperature was maintained at 0 - 5°. A 500 ml flask with condenser, magnetic stirrer, thermometer, dropping funnel, and resting in an ice-bath was charged with p-phenetidine (25.0 g; 0.182 mole) and dilute HCl (30 ml con. HCl and 40 ml H_2O). While maintaining the temperature of this second flask at 0 - 5°, sodium nitrite solution (12.6 g; 0.18 mole in 40 ml water) was added dropwise. Anhydrous sodium carbonate was added until the mixture was neutralized. The diazotized solution was added during a twenty minute period to the vigorously stirred cyanide solution with the temperature kept below 10°. After one hour of stirring at 5°, the solution was warmed to room temperature over 5½ hours. The mixture was heated to 50° C for two hours. The product was extracted with several portions of benzene and the solvent evaporated leaving a dark, thick material. This was subjected to sublimation to give a yellow solid, mp 65-68 (lit.[34] mp 69).

IV. SPECTROSCOPIC DATA

The nmr spectra were obtained by Mr. Charles D. Schaeffer, Jr. and Mr. Richard H. Tuck of Franklin and Marshall College using a Varian A-60A nmr spectrometer equipped with a Hewlett-Packard Model 200 CD audio oscillator and Model 521 C electronic counter. Standard side-banding techniques were employed with a probe temperature of 40±3°C. Coupling constants are believed accurate to within ±0.2 hertz, chemical shifts to within ±0.3 hertz, and internal chemical shifts to within ±0.4 hertz. The values listed are the average of several tracings and, for chemical shifts, are recorded relative to tetramethylsilane (TMS) used as an internal standard. Data for some of the phenetoles, N,N-diethylanilines, and aryl-diethylphosphines synthesized during this project are not yet available.

Carbon tetrachloride was employed as the principal solvent since it should not interact with the solutes and does not possess any interfering nmr absorptions. The phosphines, however, were not studied in carbon tetrachloride since trivalent phosphorus compounds unite explosively with this "inert" solvent. Such vigorous reaction with methylene chloride and chloroform was not noted, but the poor correlations of the phosphines in these two solvents and the appearance of an additional spurious doublet in the spectra run in methylene

chloride suggest that, again, some interaction is occurring. A white solid was obtained when these compounds were added to cyclohexane; thus, benzene appeared to be the only reasonable solvent for the phosphorus compounds.

Table I records the chemical shifts for aryldimethylphosphines, aryldimethylarsines, and arylmethylsulfides in the various solvents employed. Graphs I - VI represent selected plots of these δ values against substituent σ constants for the various series.

The coupling constants recorded in Table II were determined in carbon tetrachloride with the exception of the phosphines which were studied in benzene. Graphs VII - IX show these J values as a function of sigma.

The available data for the internal chemical shift study of ethylbenzenes, phenetoles and diethylanilines are recorded in Table III. The methyl, methylene, and internal shifts recorded are extrapolated, infinite dilution values from three concentrations in carbon tetrachloride. Graphs X - XIX show each of these parameters versus the sigma constants.

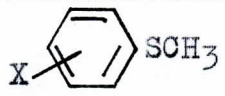
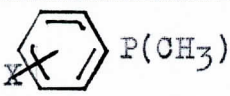
Regression analyses for these studies as well as those for the carbon, nitrogen, and oxygen analogs are recorded in Tables IV and V for chemical shifts and coupling constants respectively. Table VI lists these values for the internal shift studies.

Many of the phosphorus, sulfur, and arsenic compounds can be viewed as members of the series of toluenes, anisoles,

N,N-dimethylanilines and t-butylbenzenes. In these cases, the chemical shifts and coupling constants of the appropriate methyl groups were determined and compared to the rest of the previously studied series. These values are recorded in Tables VII and VIII for δ and J values respectively. By employing the regression analysis parameters, apparent sigma constants can be calculated from this data for the methylsulfino, dimethylphosphino, and dimethylarsino groups. Table IX lists those values derived from chemical shift data while Table X handles coupling constant data.

TABLE I

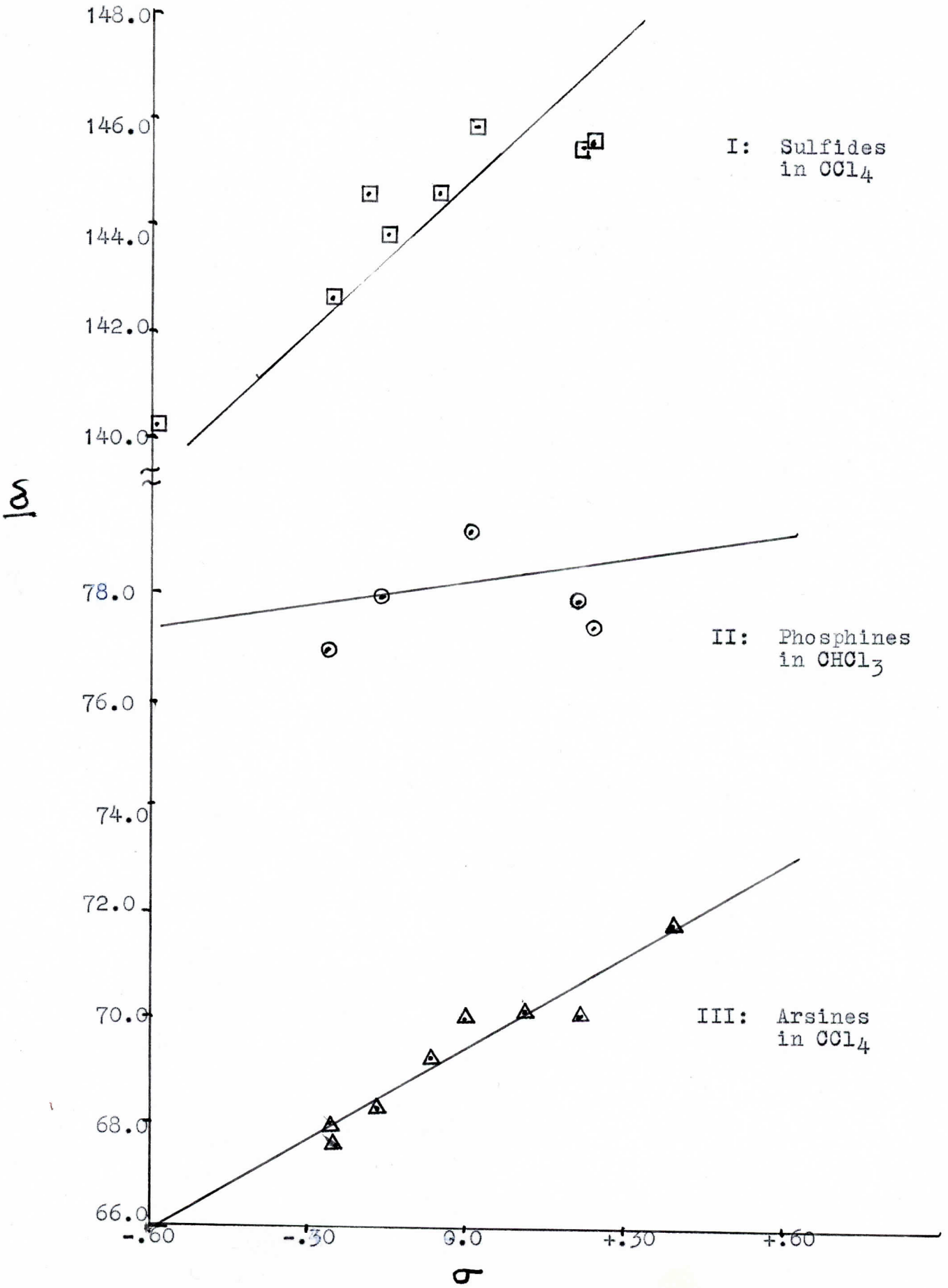
Chemical Shifts[a] for Sulfides, Phosphines, and Arsines

X	 CCl_4	$CHCl_3$	ØH	 $CHCl_3$[b]	ØH[b]	 CCl_4	$CHCl_3$	ØH
p-NO_2	152.1	152.9	102.4					
p-Cl	145.5	147.5	112.1	76.5 79.3	66.0 59.3	70.0	71.7	52.9
m-Cl						71.8	72.6	51.4
p-Br	145.6	147.0	110.6	76.0 78.9	55.4 58.7			
m-Br						71.7	72.3	50.4
p-H	145.9	148.4	119.7	77.9 80.5	63.1 66.4	70.0	72.1	59.2
p-CH_3	143.8	147.0	123.1	76.7 79.2	64.9 68.3	68.2	70.8	61.0
m-CH_3	144.6	147.6	122.3			69.2	71.5	61.4
p-t-Bu	144.6	147.6	124.9					
p-OMe	142.6	145.8	125.2	75.6 78.2	64.7 68.1	67.9	70.2	61.2
m-OMe						70.1		
p-OEt				75.4 78.0	65.2 68.2	67.6		
p-NMe_2	140.2	144.5	131.3		71.6 84.6			

a. In hertz downfield from TMS in 1% w/v or v/v.

b. The two values represent both sides of the doublet resulting from the splitting of the methyl hydrogens by phosphorus. The values plotted on succeeding graphs are the average of these two.

GRAPHS I - III
Chemical Shift Versus σ



GRAPHS IV - VI
Chemical Shift Versus σ in Benzene

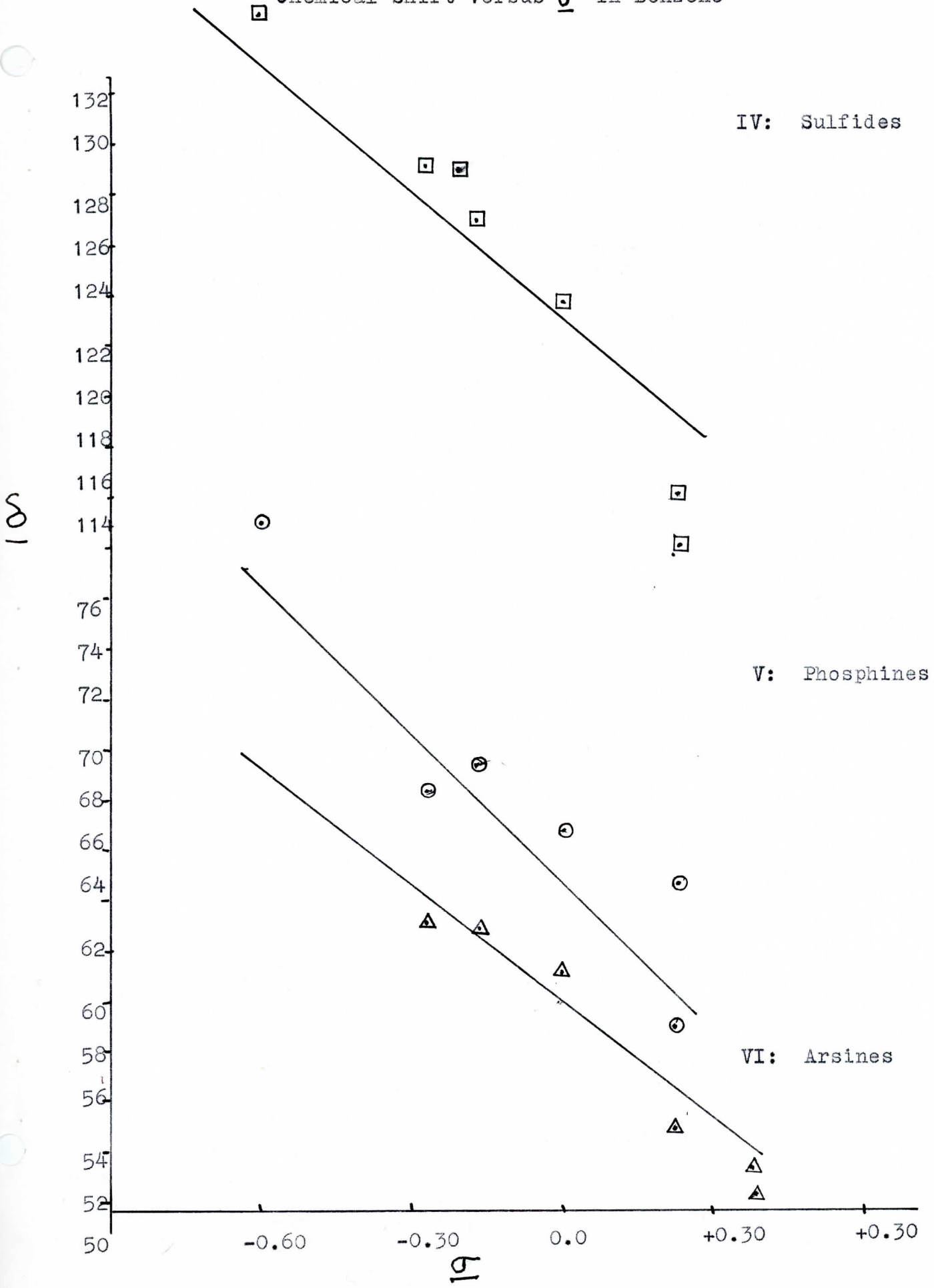
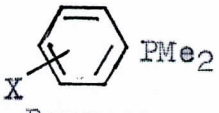
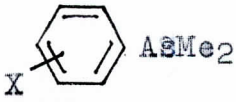


TABLE II

Coupling Constants[a] for Phosphines, Arsines, and Sulfides

X	 PMe_2 Benzene	 $AsMe_2$ CCl_4	 SMe CCl_4
p-NO_2			140.7
p-Cl	128.6	132.2	139.4
m-Cl		132.4	
p-Br	128.7		139.6
m-Br		132.4	
p-H	128.5	132.2	139.2
p-CH_3	128.2	132.3	139.2
m-CH_3		132.0	139.1
p-t-Bu			139.1
p-OCH_3	128.1	131.9	139.1
m-OCH_3		132.0	
p-OEt	127.8	132.0	
p-$N(CH_3)_2$	128.0		138.9

a. In hertz for 30% v/v or w/v

GRAPHS VII - IX
Coupling Constant Versus σ

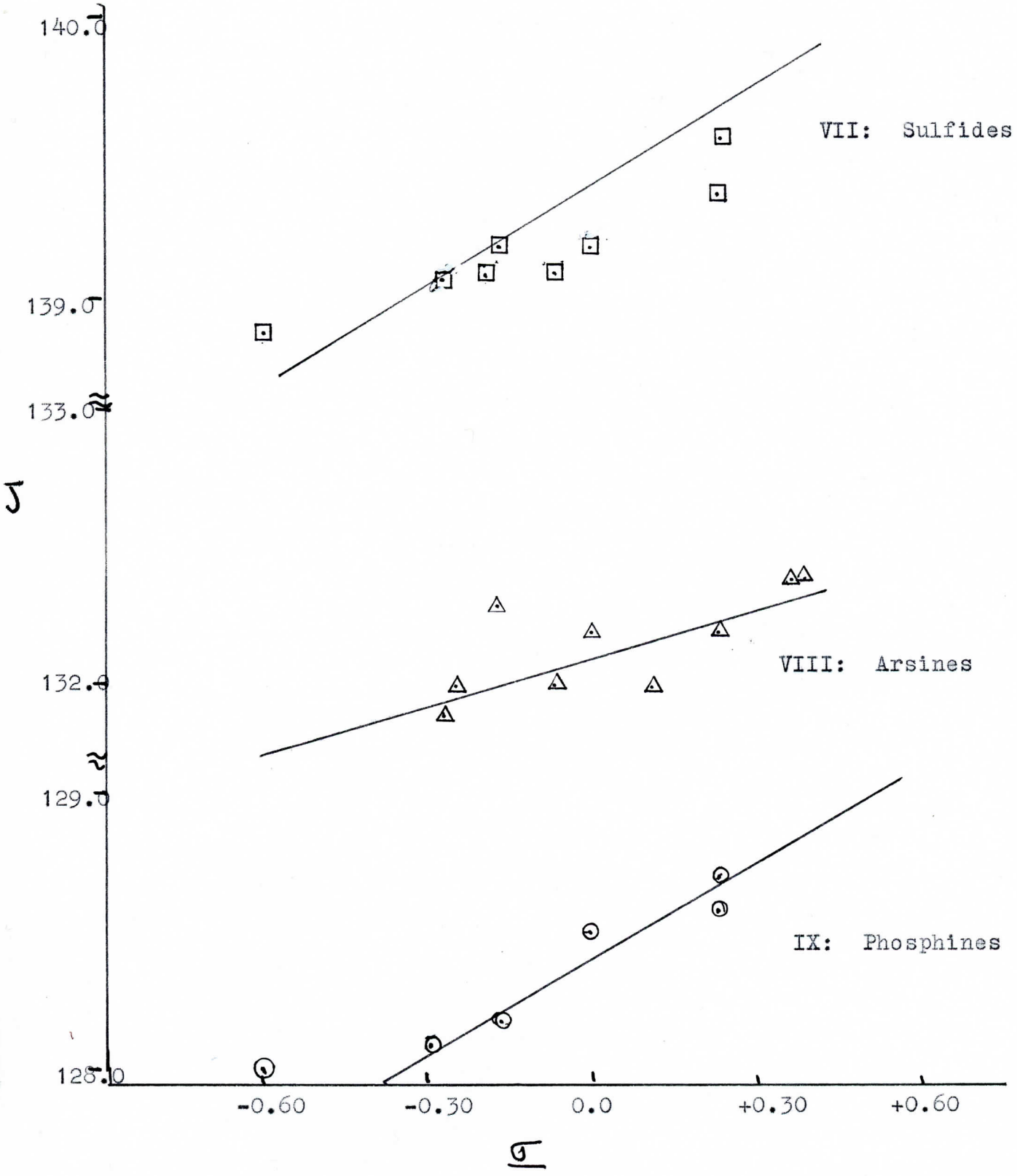
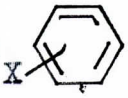


TABLE III

Internal Chemical Shifts[a] for Ethylbenzenes, Diethylanilines, and Phenetoles

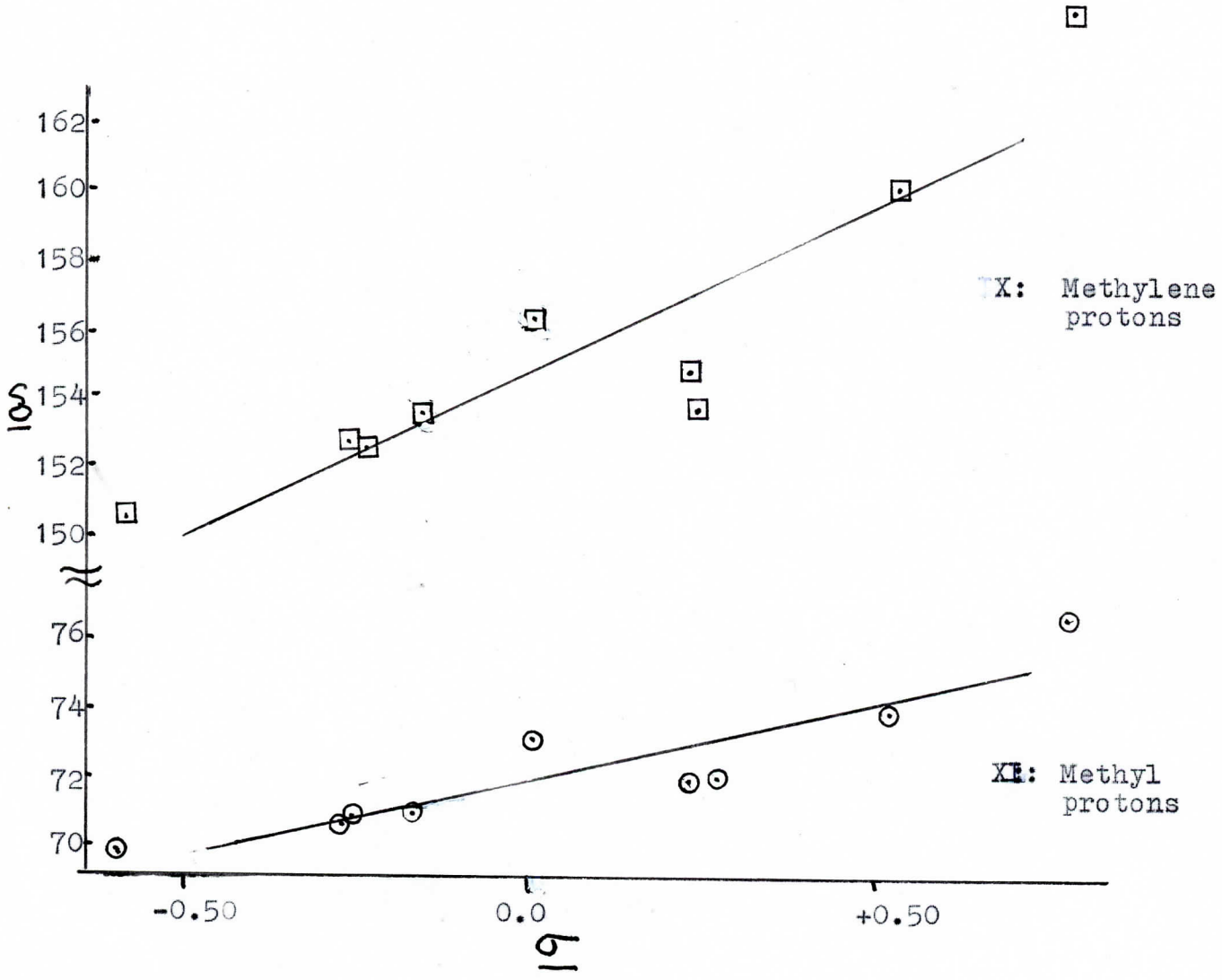


X	δCH_3	δCH_2	Δ	δCH_3	δCH_2	Δ	δCH_3	δCH_2	Δ
p-CHO				71.4	204.4	132.8	85.3	244.0	158.9
p-NO_2	76.7	165.2	88.3				86.9	246.2	158.5
p-CN				70.7	203.1	132.4			
p-CH_3CO	74.1	160.2	86.1						
p-Cl	72.0	154.7	83.1	67.6	197.6	130.1	82.3	235.5	153.9
p-Br	71.9	153.6	82.5	67.6	197.3	130.1	82.1	235.5	153.7
p-I							82.2	235.5	154.2
m-Cl				68.4	197.7	130.0			
m-CH_3				66.5	196.1	130.2	81.2	235.5	154.6
p-H	73.1	156.4	83.6	67.6	198.0	130.0	82.4	237.0	154.8
p-CH_3	71.1	153.3	82.0	65.6	195.2	129.2	80.0	233.3	154.5
p-Et							81.1	234.7	154.7
p-OCH_3	70.8	152.7	81.8	63.9	191.5	127.9			
p-OEt	70.9	152.6	82.0	63.4	190.5	127.4			
p-NMe_2	69.8	150.4	80.7						
p-NEt_2							79.1	232.1	153.0

a. In hertz for 60 Mhz. in 10% CCl_4

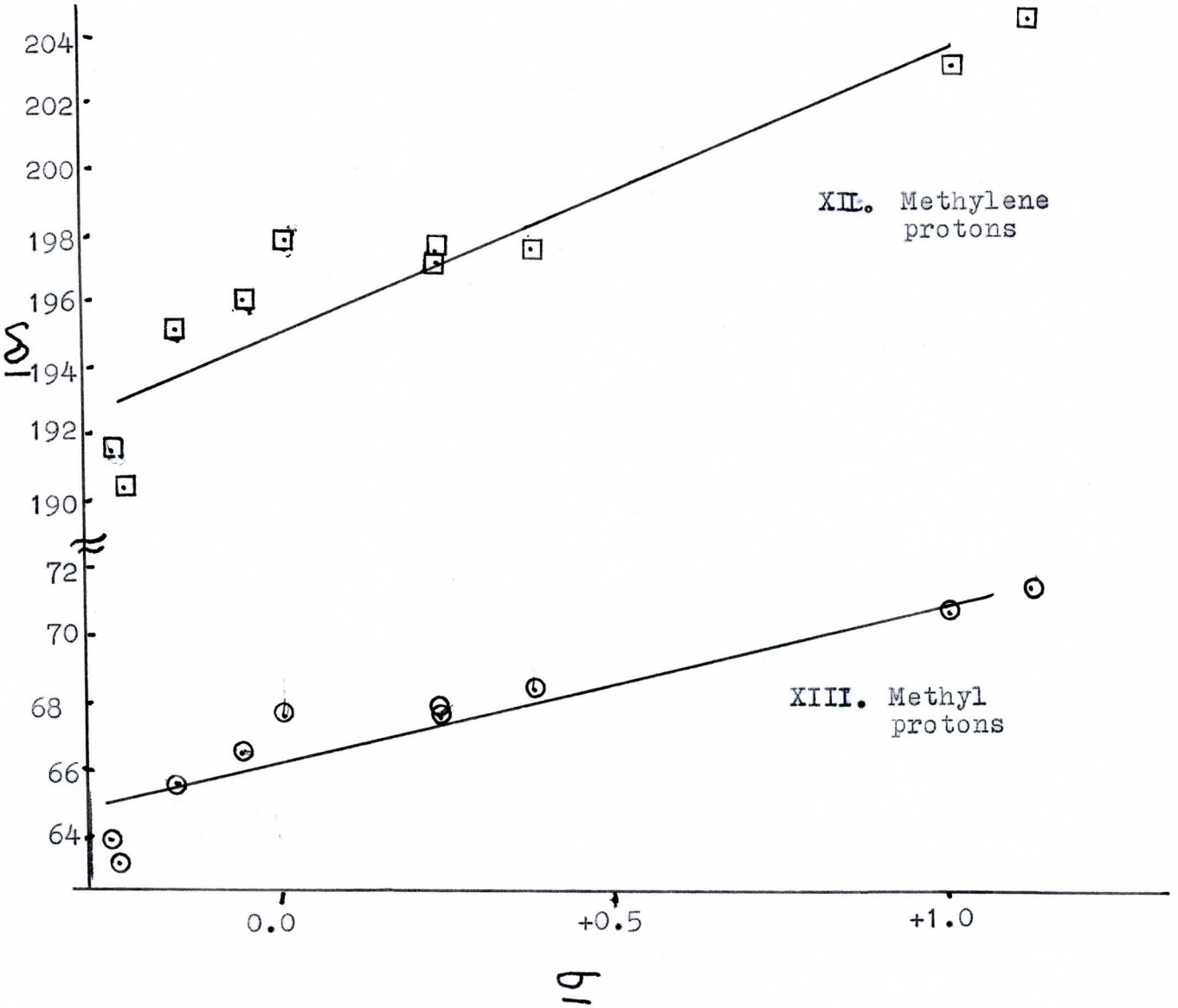
GRAPHS X AND XI

Chemical Shift Versus σ for Ethylbenzenes



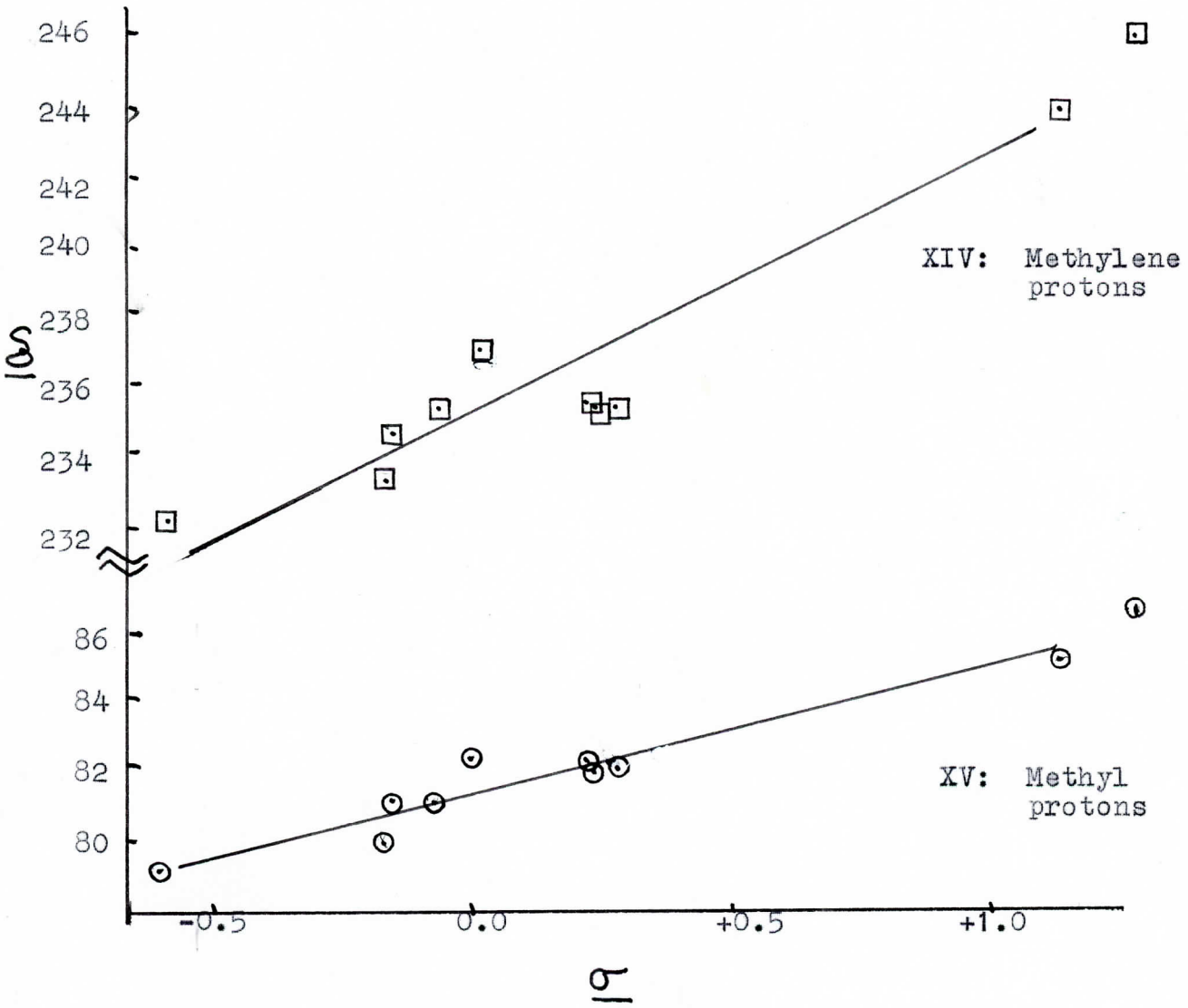
GRAPHS XII AND XIII

Chemical Shift Versus σ for Diethylanilines



GRAPHS XIV AND XV

Chemical Shift Versus σ for Phenetoles



GRAPHS XVI - XVIII

Internal Chemical Shift Versus σ for Phenetoles, Diethylanilines And Ethylbenzenes

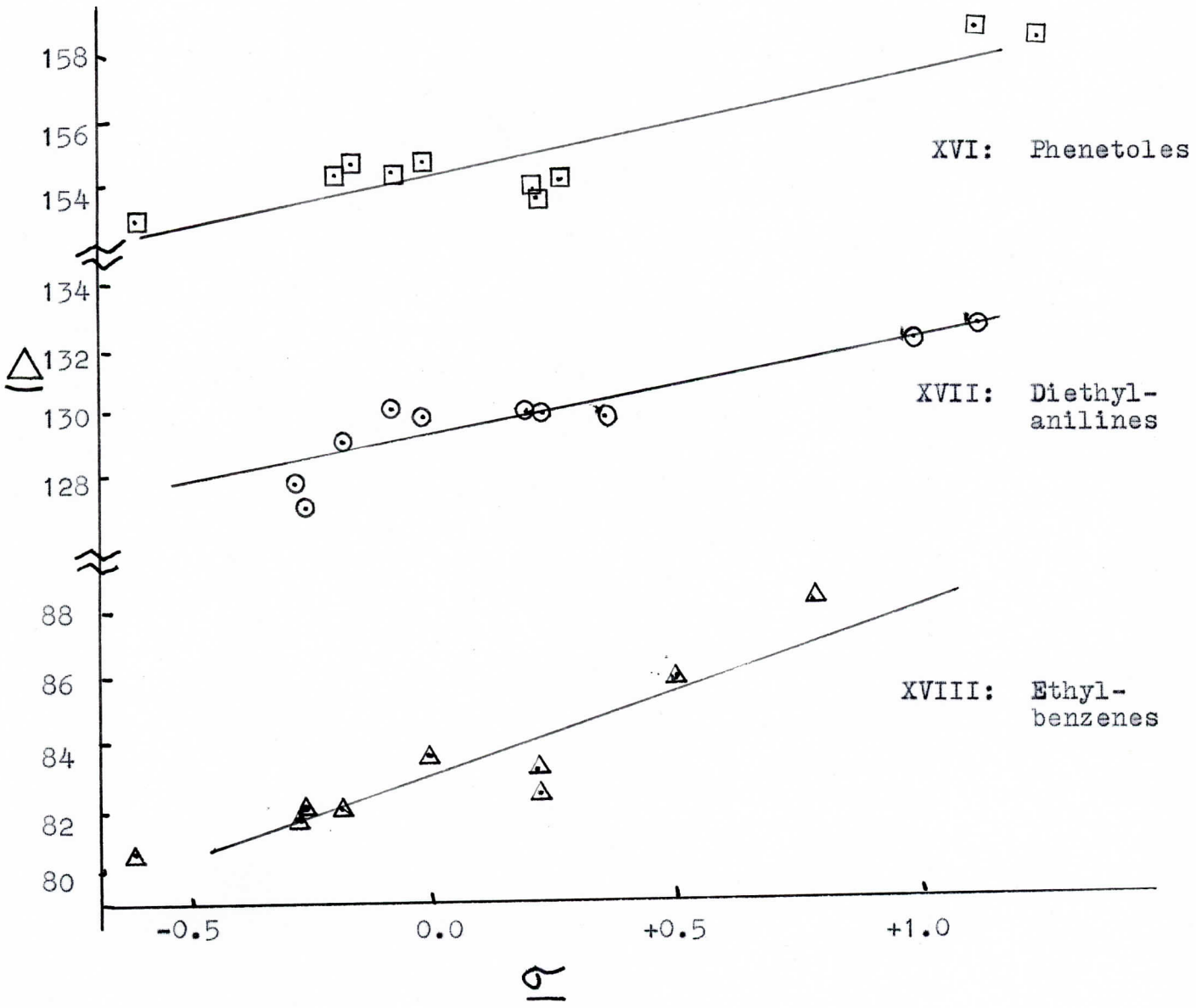
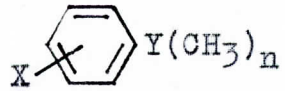


TABLE IV

Chemical Shift Regression Analysis Parameters



Y	sol.	ρ, hz.[a]	C, hz.[a]	r[b]	S[c]	n[a]
C	CCl_4	4.56	78.3	0.946	0.752	7
N	CCl_4	9.59	173.9	0.964	1.50	9
P	CH_2Cl_2	3.33	76.7	0.703	1.20	6
P	$CHCl_3$	0.687	77.9	0.183	0.966	5
P	C_6H_6	-23.4	62.8	0.979	1.76	6
As	CCl_4	5.79	69.4	0.968	0.403	9
As	$CHCl_3$	2.81	71.4	0.875	0.449	7
As	C_6H_6	-18.3	58.0	0.966	1.42	7
O	CCl_4	10.1	6.36(τ)	0.916	0.0392	14
S	CCl_4	7.91	145.0	0.961	0.950	9
S	$CHCl_3$	5.27	147.6	0.893	1.11	9
S	C_6H_6	-22.7	118.9	0.983	1.743	9

a. From equation $\delta = \rho\sigma + C$.

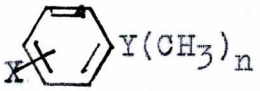
b. Correlation coefficient

c. Standard deviation of residuals

d. Number of compounds

TABLE V

Coupling Constant Regression Analysis Parameters



Y	sol.	ρ, hz.[a]	C, hz.[a]	r[b]	s[c]	n[d]
C	CCl_4	1.03	125.6	0.928	0.186	8
N	CCl_4	1.49	134.5	0.974	0.158	9
P	C_6H_6	1.16	128.4	0.993	0.0483	6
As	CCl_4	0.533	132.1	0.690	0.151	9
O	CCl_4	1.38	143.0	0.970	0.184	17
S	CCl_4	1.29	139.4	0.934	0.205	9

a. From equation $J = \rho\sigma + C$.

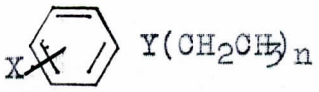
b. Correlation coefficient.

c. Standard deviation of residuals.

d. Number of compounds.

TABLE VI

Internal Shift Regression Analysis Parameters



Y	Type	ρ, hz.[a]	C, hz.[a]	s[b]	r[c]	n[d]
None	△	5.14	83.1	0.996	0.921	9
None	CH_2	9.67	155.0	2.08	0.906	9
None	CH_3	4.51	72.0	0.871	0.922	9
N	△	3.15	129.3	0.685	0.924	10
N	CH_2	8.22	195.3	1.65	0.934	10
N	CH_3	4.95	66.2	0.902	0.944	10
O	△	3.07	154.4	0.945	0.894	10
O	CH_2	7.52	235.3	1.41	0.956	10
O	CH_3	3.92	81.4	0.535	0.976	10

a. From equation $\delta = \rho\sigma + C$.

b. Standard deviation of residuals

c. Correlation coefficient

d. Number of compounds

TABLE VII

Methyl Chemical Shifts

A. Carbon Tetrachloride

Substituent	Anisoles	Toluenes	Dimethyl-anilines	t-Butyl-Benzenes
p-H	225.5	140.0	175.3	78.8
p-$As(CH_3)_2$	225.3	138.7		
m-$As(CH_3)_2$	226.3	139.9		
p-SCH_3	224.6	137.4	174.6	77.7
m-SCH_3		138.2		

B. Chloroform

Substituent	Anisoles	Toluenes	Dimethyl-anilines	t-Butyl-Benzenes
p-H	228.0	141.1		
p-$P(CH_3)_2$	228.2		180.6	
p-$As(CH_3)_2$	227.7	140.3		
m-$As(CH_3)_2$		140.8		
p-$S(CH_3)$	226.6	138.1	175.5	78.1
m-SCH_3		139.1		

TABLE VIII

Methyl Coupling Constants

Substituent	Anisoles	Toluenes	Dimethyl-anilines	t-Butyl-benzenes
p-H	143.0	125.8	134.5	125/5
p-$P(CH_3)_2$	143.7	126.0	135.4	
p-$As(CH_3)_2$	143.4	126.1		
m-$As(CH_3)_2$	143.2	126.0		
p-SCH_3	143.4	126.3	134.9	125.8
m-SCH_3		126.7		

TABLE IX

Sigma Constants from Chemical Shifts

Substituent	Anisoles	Toluenes	Dimethyl-anilines	t-Butyl-benzenes
p-$As(CH_3)_2$	+0.10	-0.02		
m-$As(CH_3)_2$	+0.21	+0.08		
p-SCH_3	+0.04	-0.12	+0.07	-0.13
m-SCH_3		-0.05		

TABLE X

Sigma Constants from Coupling Constants

Substituent	Anisoles	Toluenes	Dimethyl-anilines	t-Butyl-benzenes
p-$P(CH_3)_2$	+0.52	+0.06	+0.60	
p-$As(CH_3)_2$	+0.29	+0.12		
m-$As(CH_3)_2$	+0.15	+0.06		
p-SCH_3	+0.29	+0.23	+0.27	+0.19
m-SCH_3		+0.46		

V. RESULTS

An examination of the regression analysis correlation coefficients suggests that in these studies linear relationships have, with a few exceptions, been established for each of the three nmr parameters (δ, J, Δ) with Hammett σ constants. The lack of linearity for the phosphines in methylene chloride or chloroform can be readily explained by the solvent interactions previously discussed. The chemical shift correlation in chloroform for the sulfides and arsines is also less than might be desired. Again, solvent-solute interaction arguments might be invoked: the "acidic" hydrogen in chloroform may be involved in hydrogen bonding with the unshared electrons found on both sulphur and arsenic. Good to excellent results for δ have been obtained for both carbon tetrachloride and benzene.

The dimethylarsines failed to produce a good correlation for coupling constant data. The minimal change in these values observed for this series suggests that the differences in J are too small to be well-handled by this technique. Thus, the apparent low transmittivity of the arsenic atom might represent the limit of the use of this nmr parameter with sigma constants.

An investigation of the parameters for the ethyl compounds shows an interesting result. The use of the "internal chemical shift" did not produce better correlations than the

other techniques previously employed. Thus, at least for the ethylbenzenes, diethylanilines, and phenetoles, the use of this Δ value is apparently not to be preferred to chemical shifts or coupling constants. However, it is conceivable that for the larger atoms, for instance phosphorus or arsenic, the anisotropy effects might be more pronounced. As anisotropy increases, better correlation with internal shift than with chemical shift may be noted.

Comparisons of the magnitudes of the slopes obtained for those series which yielded satisfactory correlations can be used to evaluate the relative transmittivities of the particular "Y" atoms in structures of type 1 or 2. The chemical shift data in CCl_4 suggests an order of O>S; N>As; and S>As. The questionable chloroform data would also support the conclusion that sulphur is better than arsenic in transmitting substituent effects from the aromatic system to the attached alkyl groups. The benzene chemical shift data suggests a transmitting order of P>S>As. The negative slope obtained for each series in benzene again points to the existence of a solvent-solute charge transfer or dipole-induced dipole complex[9] in these systems.

The coupling constant data shows N>P; O>S; and S$\gtrsim$P. If any faith can be placed in the arsenic coupling constant data, then P$\gtrsim$As in its ability to transfer substituent effects.

Thus, the combined data indicates that first row elements are better transmitters of effects than second row or the

least effective third row elements. Silicon and germanium, in similar studies[35], have proved less effective in the transfer of substituent effects than any of the atoms dealt with in this paper. This is expected since the absence of unshared electrons on these two atoms provides for less interactions with the aromatic system.

The internal shift studies show ethylbenzenes > diethylanilines > phenetoles. The greater transmittivity in ethylbenzenes is expected since they possess no intervening atoms between the aromatic system and the observed ethyl groups. The N > O order is supported by the coupling constant data[7] for the corresponding methyl series.

The greater transmittivity of first row elements may be rationalized by atomic size considerations. The larger size of second and third row elements provides for poorer overlap between the aromatic π electron system and the p orbitals of the heteroatom. Effective overlap is necessary for good transfer of substituent electronic effects.

The small differences between the transmittivities of the Group V and Group VI elements as opposed to the larger differences between the corresponding first, second, and third row elements suggest that oxygen and nitrogen have similar transfer effects while sulphur and phosphorus pass on effects almost equally well.

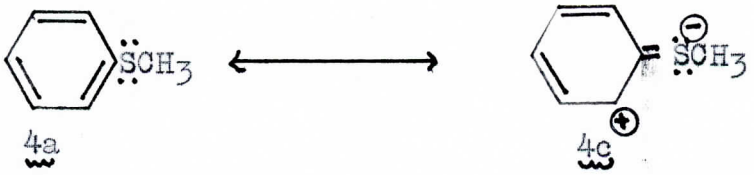
Examination of the tables (Tables VII and VIII) in which the methylsulfino, dimethylphosphino, and dimethylarsino groups are viewed as substituents on the previously studied series of toluenes, anisoles, N,N-dimethylanilines, and t-butylbenzenes makes possible an evaluation of the substituent nature of these three groups. A chemical shift greater than that for the unsubstituted parent in these series would be indicative of decreased electron density of the absorbing methyl group hydrogens while a greater coupling constant suggests more s character of the methyl C-H bonds. Thus, either a larger chemical shift or coupling constant implies that the substituent is withdrawing electrons from the aromatic system.

A comparison of Tables VII and VIII provides some confusing results. Chemical shift data, showing mostly a lower δ for the substituted compounds, suggest that these substituents are donating electrons. That is, $(p\text{-}p)_\pi$ resonance seems important. However, the coupling constants, which are greater than those of the unsubstituted parents, point to a substituent withdrawal of electrons with $(p\text{-}d)_\pi$ resonance effects important.

An analysis of the previously obtained δ versus σ plots for toluenes, anisoles, dimethylanilines, and t-butylbenzenes; however, suggests that such a comparison with the unsubstituted parents may not be justified. In many cases, the unsubstituted parent seemed to provide anomalous results,

with its value lying above the regression analysis line. Comparisons of the sigma constants obtained by using the regression analysis values would, therefore, provide a better basis of comparison since the questionable unsubstituted values are not employed directly. The chemical shift values for chlorofrom cannot be compared on this basis, since no regression parameters are available for these four series in this solvent.

The sigma constants, found in Tables IX and X, continue to provide some confusion. The chemical shift results are about equally divided between positive and negative values while the coupling constants consistently show positive constants, indicative of electron withdrawal. Since coupling constants should be less subject to solvent or anisotropic variations and since the unsubstituted parents for this nmr parameter lied on the regression lines, it seems reasonable to put more confidence in the J values. These positive constants point to the importance of (p-d)π bonding in these systems:



4a 4c

This electron withdrawal cannot be attributed to electronegativity arguments alone as demonstrated by the comparisons of the nitrogen, phosphorus, and arsenic analogs as well as the oxygen and sulphur analogs in Table XI. The electro-

negativity decrease as one proceeds down a family in the periodic table would lead to a prediction of decreased ability to attract electrons. However, the increase in magnitude of the coupling constant or chemical shift indicates more effective electron withdrawal. Thus, this data points to another factor removing electrons from the aromatic system; $(\underline{p}\text{-}\underline{d})_{\underline{\pi}}$ bonding seems the most reasonable answer.

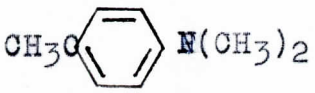
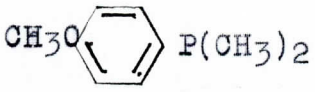
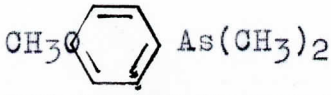
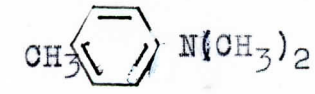
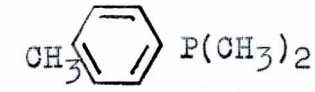
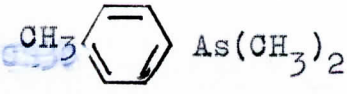
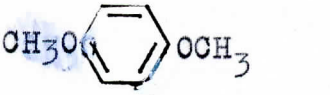
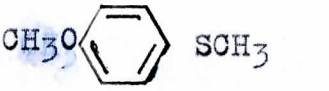
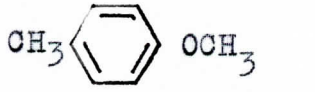
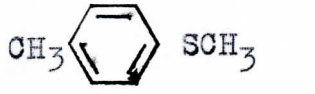
It is interesting to note that in the cases in which the parent substituent can show $(\underline{p}\text{-}\underline{p})_{\underline{\pi}}$ interactions (anisoles and dimethylanilines) the extent of $(\underline{p}\text{-}\underline{d})_{\underline{\pi}}$ interactions of the phosphorus, arsenic, or sulphur substituent appears to increase as reflected in the more positive values of the $\underline{\sigma}$ constant. This is shown not only in the J value but also in the $\underline{\delta}$ value. This is not an unexpected result and points to the importance of a dipolar resonance structure:

4a
X = OCH_3

4d
X = OCH_3

TABLE XI

Electronegativity Comparisons

δ	J	Compound	Electronegativity [a]
213	142.3		N: 3.0
	143.7		P: 2.1
225.3	143.4		As: 2.0
	125.2		N: 3.0
	126.0		P: 2.1
	126.1		As: 2.0
216	142.6		O: 3.5
224.6	143.4		S: 2.5
135.3	125.7		O: 3.5
137.4	126.3		S: 2.5

a. Values taken from Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, N.Y., 1960, p. 93.

VI. SUMMARY

This project demonstrates the study of substituent effects in some representative aromatic systems through the use of nmr parameters. Correlations of methyl chemical shifts, carbon-13 proton coupling constants, and internal chemical shifts of ethyl groups with Hammett sigma constants have proven successful.

These results have been used to evaluate the relative ability of various atoms to transmit substituent effects from the aromatic system to attached alkyl groups. Row One elements have been found more effective than Row Two or Three elements while small differences exist between Group V and Group VI elements.

An evaluation of the methylsulfino, dimethylphosphino, and dimethylarsino groups as substituents points to the importance of $(\underline{p}\text{-}\underline{d})_{\underline{\pi}}$ bonding in the systems studied.

VII. ACKNOWLEDGEMENTS

The author wishes to thank Dr. Claude Yoder, Mr. Richard H. Tuck, and Mr. Charles D. Schaeffer, Jr. of Franklin and Marshall College for providing the nmr data for this project. Financial support through a Frederick Gardner Cottrell Grant from Research Corporation is gratefully acknowledged. The advice and help of the members of the Chemistry Department is appreciated.

To Dr. Ronald E. Hess of the Chemistry Department, a very special word of appreciation is extended. His endless time, patience, and encouragement of this project have been of invaluable assistance to the author.

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